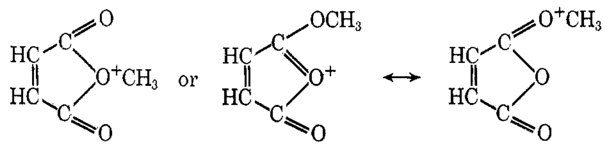
TABLE I

MASS SPECTRA OF DIMETHYL MALEATE AND FUMARATE[a]

Mass	Maleate	Fumarate
26	10.2	8.9
27	2.5	2.2
28	1.2	1.6
29	5.6	4.9
30	1.2	1.1
31	1.1	1.0
39	1.2	1.7
41	0.7	1.2
42	0.7	0.6
45	0.6	0.5
53	3.1	5.7
54	4.2	4.2
55	1.7	1.1
59	11.7	9.2
81		1.0
82	1.1	1.5
85	4.8	11.9
86		0.6
99		0.6
100		1.0
113	39.5	29.5
114	3.2	5.0
144	0.2	0.6

[a] Intensities are expressed as $\%\Sigma_{24}$.

etry, suggest that the $[M - CH_3O]^+$ ion from dimethyl maleate is stabilized by participation of an oxygen atom from the second carbomethoxy group to yield



The added stabilization apparently promotes the primary decomposition step and opposes the second one.

Such participation has a direct analogy in the mass spectra of the isomeric dimethyl phthalates, shown in Table II. Here, again, the masses of prominent peaks and supporting metastable peaks

TABLE II

PARTIAL SPECTRA OF THE ISOMERIC DIMETHYL PHTHALATES[a,b]

Mass	Ion	Ortho	Iso	Tere
135	$[M - CO_2CH_3]^+$	2.9	7.6	6.2
163	$[M - CH_3O]^+$	40.2	32.6	33.5
194	$[M]^{+\cdot}$	3.0	7.7	8.1

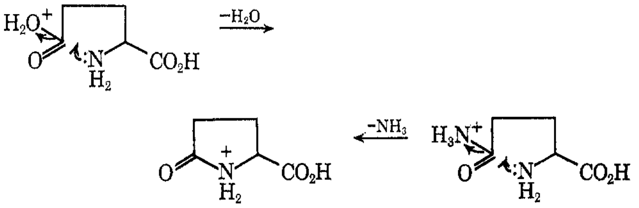
[a] Unpublished spectra, this laboratory, measured with 70-V electrons on a CEC Model 21-103 instrument. The spectra are qualitatively similar to those reported by F. W. McLafferty and R. S. Gohlke, *Anal. Chem.*, **31**, 2076 (1959). [b] Intensities are expressed as $\%\Sigma_{24}$.

$$137.1 \quad 194^+ \longrightarrow 163^+ + 31$$

and

$$111.8 \quad 163^+ \longrightarrow 135^+ + 28$$

establish sequential loss of $CH_3O\cdot$ and CO in all three isomers. Dimethyl *o*-phthalate gives a sharply higher intensity for $[M - CH_3O]^+$ and lower intensities for the molecular ion and $[M - CO_2CH_3]^+$ than the iso- and terephthalates. Thus, this set of spectra also suggests that the $[M - CH_3O]^+$ ion from the *o*-phthalate is stabilized by participation of an oxygen atom from the second carbomethoxy group. Furthermore, this participation closely parallels that apparently involved in the respective loss of H_2O and NH_3 from the protonated molecules in the chemical ionization mass spectra of glutamic acid and glutamine.[6] Other



examples of participation in electron-impact mass spectra have been described recently.[7]

Experimental Section

The methyl esters were prepared by refluxing the acids with anhydrous hydrogen chloride in methanol. The fumarate was purified by recrystallization from methanol; the maleate, by water extraction. Identities and purities were checked by ir and nmr spectra as well as by melting point of the fumarate and gas chromatography on the maleate. Titration of both esters with alcoholic potassium hydroxide established the absence of free acid.

Mass spectra were measured with 70-V electrons on a CEC Model 21-103 instrument with the inlet system and source at 350 and 250°, respectively. Another 21-103 with the inlet system at 150° gave virtually identical spectra.

Registry No.—Dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6.

(6) G. W. A. Milne, T. Axenrod, and H. M. Fales, *J. Amer. Chem. Soc.*, **92**, 5170 (1970).

(7) R. H. Shapiro and K. B. Tomer, *Org. Mass Spectrom.*, **3**, 333 (1970), and references cited therein.

Pyrolysis of 1-Nitroadamantane

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A recent study showed that adamantane decomposed at 550–570° when aluminum silicate and aluminum chromate were present as catalysts.[1a] In the absence of catalysts, it decomposed at 660–675°.[1b] Both reactions gave complex mixtures of products consisting primarily of benzene, mono- and dialkylbenzenes, substituted naphthalenes, and C_2–C_4 hydrocarbons. The present investigation was undertaken to learn more about the thermal decomposition of the adamantane nucleus, with particular emphasis on the thermal reactions of the adamantyl radical derived from 1-nitroadamantane.

This compound is a member of a group of 1-substituted adamantane derivatives that characteristically lose the substituent readily upon electron impact in the mass spectrometer.[2] The subsequent fragmentation of

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(1) (a) B. A. Kazanskiy, E. A. Shokova, and T. V. Korosteleva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **11**, 2642 (1968); (b) *ibid.*, **11**, 2640 (1968).

(2) Z. Dolejsek, S. Hala, V. Hanus, and S. Landa, *Collect. Czech. Chem. Commun.*, **31**, 435 (1966).

the adamantyl ion formed by this process might parallel the decomposition of the adamantyl radical generated by the pyrolysis of 1-nitroadamantane. If so, the mass spectrum can give some indication of how the pyrolysis products form.

1-Nitroadamantane was pyrolyzed at 500-600° to give the products shown in Table I. No reaction occurred below 500°.

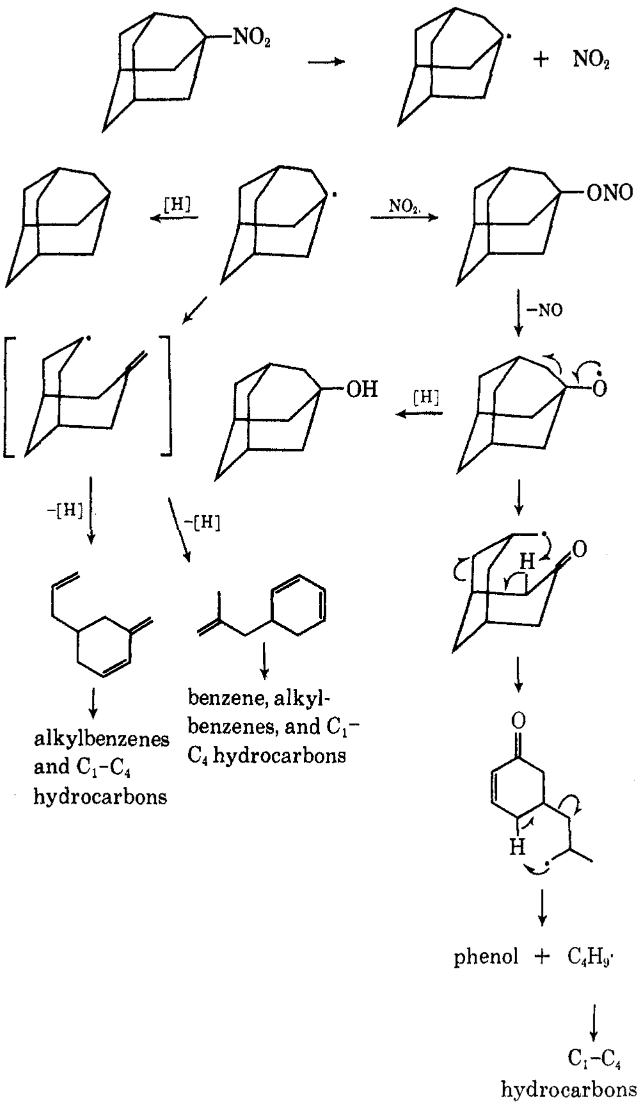
TABLE I

PYROLYSIS OF 1-NITROADAMANTANE

Conditions			
Temp, °C	500	600	600
Nitroadamantane, mol	0.027	0.030	0.030
Contact time, sec	12.9	7.1	11.1
Conversion, %	15.1	41.0	70.7
Products[a]	Yield, mol %[b]		
Benzene	0.5	0.9	2.3
Toluene	1.6	2.3	4.5
Xylenes			0.8
Phenol	6.7	16.3	18.0
Unknown, $C_{10}H_{14}$	4.4	5.1	2.4
Adamantane	18.0	13.9	12.4
Adamantanol	7.6	4.1	1.5
Gaseous products[c]	61.2	57.4	58.1

[a] Other products (combined yield less than 1%) identified by directly coupled gas chromatography-mass spectrometry were ethylbenzene, styrene, C_9 alkylbenzenes, indan, butylbenzenes, naphthalene, and cresols. These compounds were present in concentrations too low for meaningful quantitative analysis. [b] Yields were determined by gas chromatography. [c] The gaseous products consisted of methane, ethane, ethylene, propane, propylene, butane, butenes, and nitric oxide.

SCHEME I



The data in Table I suggest the order of reactions in Scheme I. The adamantyl radical derived from the decomposition of 1-nitroadamantane appears to react *via* three paths: (1) hydrogen abstraction to give adamantane, (2) back reaction with NO_2 to form the nitrite ester, which then decomposes to NO and the adamantyloxy radical, and (3) fragmentation to alkylbenzenes and C_1–C_4 hydrocarbons. The mass spectrum of the product designated "unknown, $C_{10}H_{14}$" in Table I indicated that this product was a nonaromatic $C_{10}H_{14}$ hydrocarbon, possibly a mixture of isomers. The decrease in yield of this component at higher nitroadamantane conversions is accompanied by an increase in yield of C_6–C_8 aromatic products, suggesting that the $C_{10}H_{14}$ hydrocarbons are precursors to the alkylbenzenes as well as the C_1–C_4 hydrocarbon products.

This predominant formation of C_6 and C_7 hydrocarbons from decomposition of the adamantyl radical at higher conversions closely parallels the fragmentation of the adamantyl ion generated by electron impact on 1-nitroadamantane. The partial mass spectrum of 1-nitroadamantane is summarized in Scheme II. Reaction steps supported by metastable peaks are denoted by solid arrows; relative intensities, uncorrected for naturally occurring heavy isotopes, are expressed as percentages of total ionization above mass 25 and are enclosed in parentheses. The ions that can be identified as decomposition products of $C_{10}H_{15}^+$ (presumably formed as the adamantyl ion) consist largely of C_6 and C_7 species.

There is, of course, no mass spectral parallel for the formation of adamantane, as it involves a bimolecular hydrogen abstraction by the adamantyl radical. The decreasing yield of adamantane with increasing 1-nitroadamantane conversion in pyrolysis shows that the adamantyl radical prefers either to rearrange with loss of hydrogen to give $C_{10}H_{14}$ or to react with NO_2 to give the adamantyloxy radical at higher temperatures and/or longer contact times. The decrease in yield of adamantane cannot be attributed to its thermal decomposition since adamantane was found to be stable at the temperatures employed in this work.

The adamantyloxy radical may arise by the reaction of the adamantyl radical with NO_2 or by a nitro–nitrite rearrangement of nitroadamantane, paralleling the thermal reaction of nitrobenzene.[3] The analogous ionic product, $C_{14}H_{15}O^+$, in the mass spectrum of 1-nitroadamantane presumably arises by such a nitro–nitrite rearrangement. Hydrogen abstraction by the adamantyloxy radical gives adamantanol. The partitioning of the adamantyloxy radical between phenol and adamantanol favors phenol at higher temperatures and longer contact times as evidenced by the increase in yield of phenol and the corresponding decrease in yield of adamantanol. Phenol could also form from the reaction of NO_2 with benzene.[3] However, this would seem to be a minor reaction since toluene is formed in greater yields than benzene and only small quantities of cresols are

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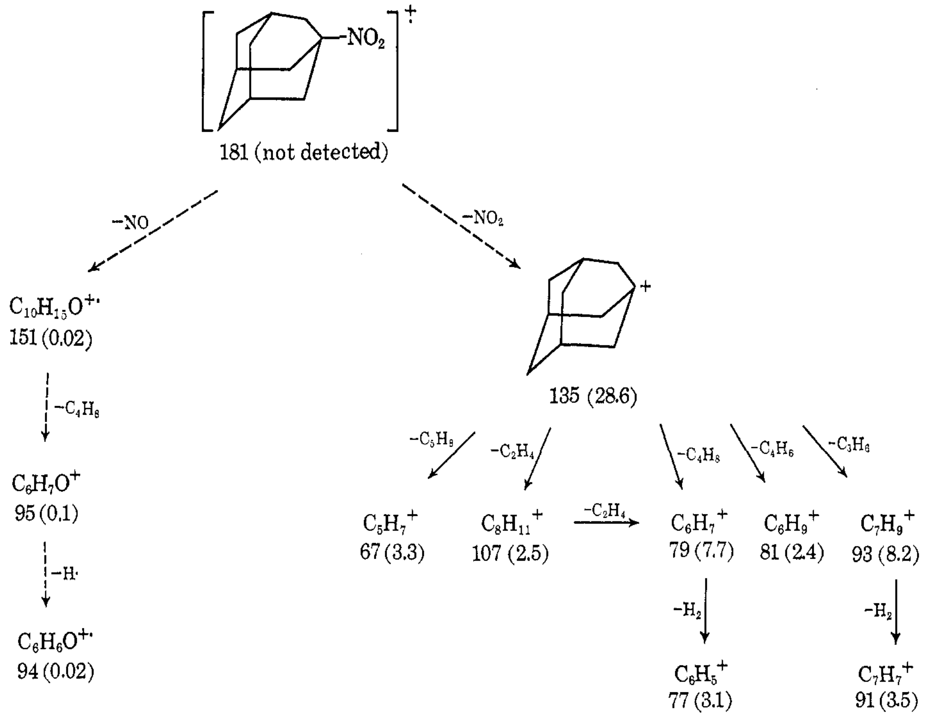
[3] E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967).

Scheme II



produced. The postulate that phenol is formed by the decomposition of the adamantyloxy radical finds a parallel in the mass spectrum of 1-adamantanol, in which the most abundant ion is $C_6H_7O^+$ (mass 95) formed by loss of $C_4H_9\cdot$ from the molecular ion.[2]

The product distribution from the pyrolysis of 1-nitroadamantane differs from that of adamantane[1] in that the latter produced substantial amounts of naphthalene and alkylnaphthalenes. These products presumably stem from initial carbon–carbon bond cleavages leading to reaction intermediates other than those derived from the adamantyl radical. The gaseous products also differ in that no methane was observed from the pyrolysis of adamantane,[1] whereas methane was one of the major gaseous products from the thermal decomposition of 1-nitroadamantane. This absence of methane is surprising since methylnaphthalenes were reported as products.

We are presently studying the reactions of adamantyl radicals formed *via* hydrogen abstraction by alkyl and aryl radicals derived from nitro derivatives at elevated temperatures.

Experimental Section

1-Nitroadamantane.—To a stirred solution of 123 ml of 40% peracetic acid and 450 ml of benzene was added over a 60-min period 30 g (0.2 mol) of 1-aminoadamantane in 300 ml of benzene. The solution was then heated under reflux for 3 hr and poured into 500 ml of water. The organic layer was separated, washed twice with 200 ml of 10% aqueous sodium hydroxide and 200 ml of 10% hydrochloric acid, and then washed with 100 ml of water. The benzene solution was dried over sodium sulfate. Evaporation of the benzene gave 28 g of crude product which was recrystallized from methanol to give 24 g (67% yield) of 1-nitroadamantane, mp 157–158° (lit.[4] mp 158.5–159°).

The pyrolysis reactions were run in a Vycor tube filled with Vycor chips in an electric furnace under pure dry nitrogen with contact times of 7–13 sec. The vapors were condensed in a flask at 0° and samples of the uncondensed effluent gases were collected for mass spectral analysis. The reaction tube was washed with chloroform, which was later removed by distillation. The condensates and the residues from the chloroform washes were analyzed by gas chromatography and directly coupled gas chromatography–mass spectrometry.[5]

In a typical experiment, 1-nitroadamantane (5.45 g, 0.030 mol) was passed through a Vycor tube at 600° under a nitrogen flow of 20 cc/min with a contact time of 11.1 sec. The 1-nitroadamantane was introduced into the reaction tube by boiling it in a bulb connected to the tube and having the nitrogen sweep the vapors into the reaction zone. The vapors were condensed in a flask at 0° (2.17 g). A sample of the uncondensed effluent gases was collected for mass spectral analysis halfway through the reaction. The reaction tube was washed with chloroform which was removed by distillation to give 0.60 g of residue. The condensate and the residue were then analyzed by gas chromatography and directly coupled gas chromatography–mass spectrometry. The column used in the gas chromatography work consisted of 10% OV 17 on Chromosorb W.

Mass Spectrometry.—The mass spectrum of 1-nitroadamantane was measured with 70-V electrons on a Consolidated Model 21-103 instrument, with the source at 250° and the inlet system at 150°. At inlet temperatures above 200°, thermal degradation of the sample occurred.

Registry No.—1-Nitroadamantane, 7575-82-8.

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[4] G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961).

[5] E. K. Fields and S. Meyerson, *ibid.*, **33**, 4487 (1968).

Electronic Effects of a Phosphorane Substituent[1]

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Taft and his coworkers have shown that the ^{19}F chemical shifts of *m*- and *p*-fluoro-substituted aromatics

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